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ORIGINAL CONTRIBUTION

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Electron transfer quenching of tris(2,2′-bipyridine) ruthenium (II) complex derivatives covalently linked to poly(*N*-isopropylacrylamide) in aqueous solutions

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Abstract Tris(2,2′-bipyridine) ruthenium(II) complex, ionic probe, was incorporated into poly(*N*-isopropylacrylamide) (PNIPA), which is known to be a thermoresponsive polymer, by a copolymerization method. Electron transfer quenching of the complex probe by methyl viologen was investigated as a function of temperature. The electron transfer quenching rate constant (k_q) in a globular state (higher temperature than the LCST (31 °C)) is 4–5 times as large as that in a coil state (lower temperature) from the Stern–Volmer analysis. The result is quite different from the quenching of pyrene probe incorporated into PNIPA in the previous study. This is because hydrophilic ruthenium probe is located at the interface of polymer globular matrix even in a globular state, whereas pyrene probe was embedded into the hydrophobic matrix. The quenching behavior is discussed by a difference in molecular environment of the probes in phase transition of PNIPA in the aqueous solution.

Key words Poly(*N*-isopropylacrylamide) – tris(2,2′-bipyridine) ruthenium(II) complex – electron transfer – thermoresponsive polymer – phase transition

Introduction

Various ruthenium complexes like tris(2,2′-bipyridine) ruthenium(II) complex(Ru(bpy)$_3^{2+}$) have been attracting much attention as photoredox species for application to solar energy conversion to a storable form of energy and for photocatalytic reduction of carbon dioxide [1–7]. Since Ru(bpy)$_3^{2+}$ has a large molar absorption coefficient in a visible light region and the excited state performs oxidative and reductive electron transfer to various acceptors and donors, the energy conversion systems coupled with the photoinduced electron transfer of the ruthenium complex have been proposed by many workers. Rapid back electron transfer (charge recombination), however, in homogeneous solutions makes it difficult to realize the energy conversion system. Therefore various microscopic heterogeneous molecular assemblies such as micelle have been utilized for a design of effective photoinduced electron transfer systems. We have continued to investigate the electron transfer reaction in microscopic heterogeneous assemblies, such as micelles, microemulsions, polyelectrolyte and Langmuir–Blodgett films [8–18].

Recently, amphiphilic polymers having a drastic conformational change by external physical stimulation have received a growing interest as a new fascinating molecular assembly. Poly(*N*-isopropylacrylamide) (PNIPA) is known to be a typical thermoresponsive polymer and exhibits a reversible coil-globule phase transition at about 31 °C, (T_C), which is defined as a lower critical solution temperature (LCST). The polymer has an extended coil conformation at lower temperature than LCST, while at higher temperature the chain transforms into a collapsed globular state. The environment change by the coil-globule transition of PNIPA have been investigated by using various probes. Winnik revealed that physical environmental changes are induced with conformation change by fluorescence technique using PNIPA labeled with polycyclic aromatic compounds [19–22]. There are, however, few studies on the influence of environment change induced by the coil-globule transition on photoinduced electron transfer reactivity. In the previous work we studied electron transfer quenching of pyrene chromophore covalently linked to polymer (PNIPA-Py) by ionic or amphiphilic quenchers [23]. It was revealed that hydrophobic pyrene chromophore is rigidly embedded into polymer matrix and the quenching efficiency by ionic quenchers is reduced drastically in the globular state.

In this work, we prepared a thermoresponsive polymer (PNIPA-Ru) of NIPA with $Ru(bpy)_3^{2+}$ derivatives as an ionic probe to investigate the effect of the polymer conformation change upon the electron transfer quenching of $Ru(bpy)_3^{2+}$ by methyl viologen (MV^{2+}) in aqueous solutions.

Experimental section

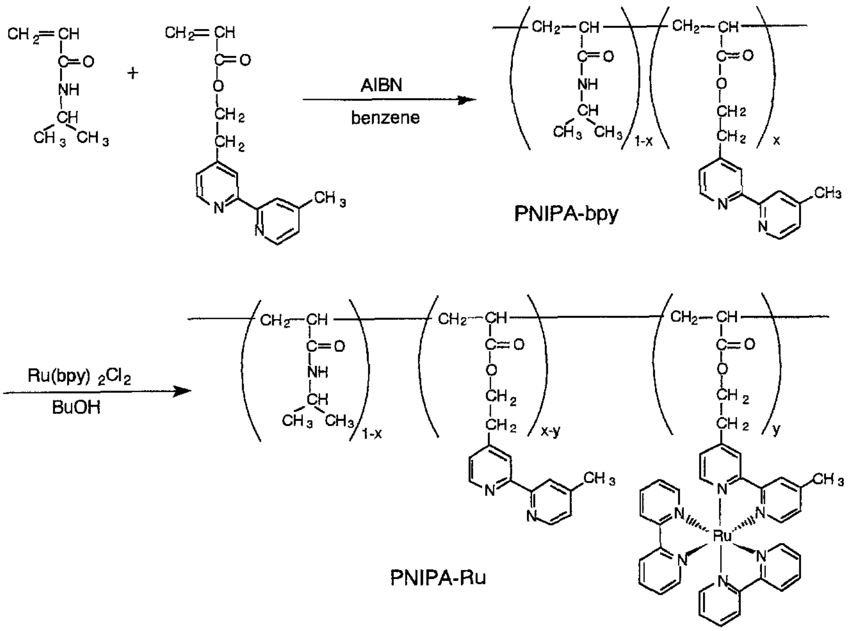
Materials

NIPA, provided by Eastman Kodak Co., was purified by recrystallization from a benzene/*n*-hexane mixture to remove inhibitor and impurities. Water for polymer aqueous solutions was purified with a Millipore Milli-Q system. 2-(4-(4′-Methyl-2,2′-bipyridyl))ethylacrylate monomer was prepared with a modification of the procedure of Spiro and Ghosh [24]. 4,4′-Dimethyl-2,2′-bipyridine was lithiated by an equimolar amount of lithium diisopropylamide (LDA) in THF and treated with an excess of gaseous formaldehyde. The reaction was then quenched by addition of water to yield 4-(hydroxyethyl)-4′-methyl-2,2′-bipyridine. 4-(Hydroxyethyl)-4′-methyl-2,2′-bipyridine was reacted with acryloyl chloride in dichloromethane in the presence of triethylamine and then the product, 2-(4-(4′-methyl-2,2′-bipyridyl))ethylacrylate was purified by recrystallization.

Synthesis of PNIPA-Ru

PNIPA-Ru was prepared by a reaction of bipyridine ligand polymer (PNIPA-bpy) with $Ru(bpy)_2Cl_2$ as shown in Scheme 1. A 1-butanol solution (150 ml) of PNIPA-bpy (500 mg) and $Ru(bpy)_2Cl_2$ (100 mg) was refluxed for 60 h. The resulting solution was poured into *n*-hexane and the polymer was precipitated. The polymers were purified by reprecipitation from a filtered chloroform solution into a large excess of *n*-hexane and dried under vacuum at room temperature. PNIPA-bpy was prepared by radical copolymerization of NIPA with 2-(4-(4′-methyl-2,2′-bipyridyl))ethylacrylate in benzene at 60 °C using AIBN as a radical initiator. The weight-average molecular weight

Scheme 1



(M_w) of PNIPA-Ru was determined to be $M_w = 320\,000$ by GPC measurement. The copolymer composition of PNIPA-Ru was determined by UV/vis absorption spectrum using the molar absorption coefficients of 2,2′-bipyridine ($\varepsilon_{283} = 14,400\,\mathrm{l \cdot mol^{-1} \cdot cm^{-1}}$) and Ru(bpy)$_3^{2+}$ ($\varepsilon_{452} = 14,600\,\mathrm{l \cdot mol^{-1} \cdot cm^{-1}}$), respectively.

Measurements

The coil-globule transition temperature was measured with differential scanning calorimetry (DSC) (SSC-5000, DSC-100 (SEIKO, Co.)). UV/vis absorption spectra were measured with a Hitachi U-3000 spectrophotometer. Steady-state fluorescence emission spectra were recorded with a Hitachi F-4500 spectrophotometer. The temperature of the water-jacketed cell holder was controlled with a circulating bath. The temperature drift was within 0.1 °C. All sample solutions were bubbled with N_2 to remove O_2. The emission decays were measured by time-correlated single-photon counting method using Ultrafast Reaction Analyzer System at Institute for Chemical Reaction Science of Tohoku University described elsewhere [25].

Results and discussions

Characterization of PNIPA-Ru

The contents of the uncoordinated bipyridylethylacrylate monomer and Ru(bpy)$_3^{2+}$ complex in PNIPA-Ru were determined to be 1.7 and 1.9 mol%, respectively by electronic absorption spectroscopy. It is known that the coil-globule phase transition of PNIPA in aqueous solutions is observed clearly in DSC measurement as an endothermic peak around 31 °C (Fig. 1) [26, 27]. PNIPA-Ru also clearly shows an endothermic peak, which can be assigned to the coil-globule transition, around 31 °C in the DSC curve (Fig. 1). The thermoresponsive behavior of PNIPA is not changed by incorporation of this small amount of ionic probe, whereas the transition heat is slightly varied (Table 1). In general, incorporation of hydrophilic groups into PNIPA causes the transition temperature (T_C) to shift to higher temperature. The reason why the T_C is PNIPA-Ru was not shifted much even though there was incorporation of a hydrophilic Ru(bpy)$_3^{2+}$ is not clear in the present work. A possible explanation is as follows; the content of Ru(bpy)$_3^{2+}$ is very small (1.9 mol%) and hydrophobic 2-(4-(4′-methyl-2,2′-bipyridyl) ethylacrylate) (1.7 mol%), which is not coordinated with Ru(bpy)$_2$Cl$_2$, is balanced with the hydrophilic property and then overall hydrophobic-hydrophilic balance of the polymer is not changed. In the subsequent section, as the property of PNIPA in a coil form and a globular form, we measured the properties of ruthenium complex probe incorporated into PNIPA-Ru at 15° and 40 °C, respectively.

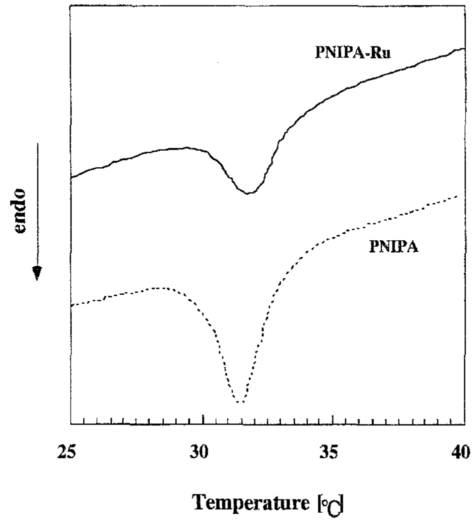


Fig. 1 DSC heating curves of PNIPA-Ru and PNIPA in aqueous solutions. Scanning rate; 1 °C/min

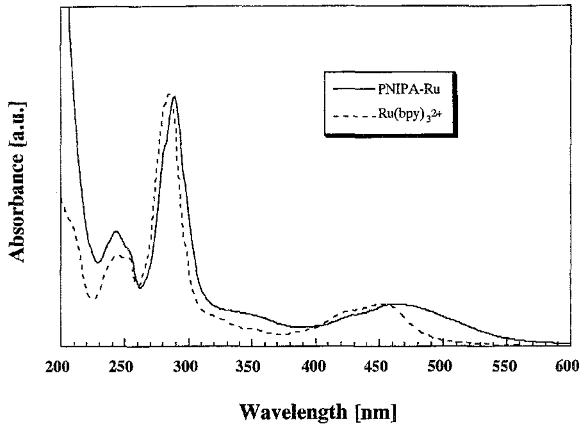


Fig. 2 UV/vis absorption spectra of PNIPA-Ru and of Ru(bpy)$_3^{2+}$ in aqueous solutions

Table 1 DSC data of PNIPA and PNIPA-Ru

	Transition Temperature [°C]	Transition Heat [mJ/mg]
PNIPA	30.03	0.6
PNIPA-Ru	30.06	0.4

The absorption spectrum of PNIPA-Ru shows an intense absorption at around 450 nm which can be assigned to metal-to-ligand charge transfer band (MLCT) of Ru(bpy)$_3^{2+}$ (Fig. 2). The emission spectrum composed of

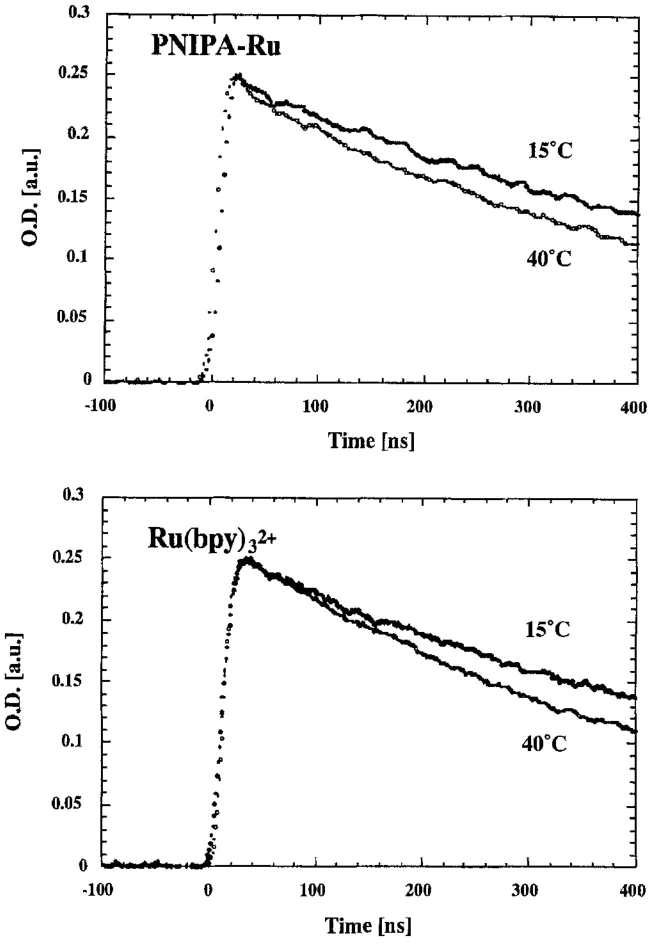


Fig. 3 Emission decay profiles of PNIPA-Ru and $Ru(bpy)_3^{2+}$ in aqueous solutions monitored at 600 nm. Laser excitation:450 nm

the broad emission at around 600 nm also supports the introduction of $Ru(bpy)_3^{2+}$ moiety into PNIPA as a good emission probe. The emission decays of the excited $Ru(bpy)_3^{2+}$ moiety in PNIPA-Ru and $Ru(bpy)_3^{2+}$ aqueous solutions at 15° and 40 °C are measured using the time-correlated single-photon-counting method (Fig. 3). The emission decays monitored at 600 nm obeyed the first-order kinetics and the lifetimes are collected in Table 2. The lifetime in PNIPA-Ru in the globular state (40 °C) is shorter than that in the coil state (15 °C). This temperature dependency of the lifetime, however, is quite the same with $Ru(bpy)_3^{2+}$ complex in water. It is clear that the lifetime of Ru complex in PNIPA-Ru is not influenced by the coil-globule phase transition. This result is very different from the behavior of pyrene probe in PNIPA-Py where the lifetime of the pyrene probe increased drastically at the phase transition [23]. The increase in the lifetime in PNIPA-Py, which is correlated with emission intensity enhancement in the globular state, can be explained by the suppression of thermal deactivation processes of pyrene probe, due to a restriction of molecular motion in the globular state. It is confirmed that the pyrene probe is embedded in a rigid polymer matrix in the globular state from the measurement of depolarization of the pyrene fluorescence. The present behavior of Ru complex probe in the coil and globular state indicates that the Ru-probe places in a relatively hydrophilic region even in the globular state.

Table 2 Emission lifetimes (τ) and Stern–Volmer constants (K_{SV}) for PNIPA-Ru and $Ru(bpy)_3^{2+}$

		$\tau[s]$	K_{SV} [M^{-1}]	k_q [$s^{-1}M^{-1}$]
PNIPA-Ru	15 °C	6.49×10^{-7}	240.1	3.70×10^8
	40 °C	5.25×10^{-7}	782.3	14.9×10^8
$Ru(bpy)_3^{2+}$	15 °C	6.25×10^{-7}	181.3	2.90×10^8
	40 °C	4.42×10^{-7}	198.9	4.50×10^8

Electron transfer quenching

It is known that the emission of the excited $Ru(bpy)_3^{2+}$ is quenched by methyl viologen (MV^{2+}) via electron transfer mechanism, as follows

$$Ru(bpy)_3^{2+*} + MV^{2+} \rightarrow Ru(bpy)_3^{3+} + MV^{+} \ . \qquad (1)$$

The electron transfer quenching for PNIPA-Ru in aqueous solutions at the coil and globular state was investigated by Stern–Volmer analysis. The relative emission intensity (I/I_0) of the excited Ru complex in the absence (I_0) and in the presence (I) of MV^{2+} quencher is plotted against the MV^{2+} concentration for PNIPA-Ru and $Ru(bpy)_3^{2+}$ in Fig. 4. The Stern–Volmer plots for low molecular weight $Ru(bpy)_3^{2+}$ complex in water show almost the same quenching efficiency at 15° and 40 °C. In the case of PNIPA-Ru, however, the plots indicate that the quenching efficiency at 40 °C (globular state) is larger than that at 15 °C (coil state). In the quenching of PNIPA-Ru at 15 °C the Stern–Volmer plots deviate from a linear line and show an upward curve at the region of over 0.005 M MV^{2+}. It is known that PNIPA shows a conformational change not only by the thermal stimulation, but also by additive, such as salt, surfactant, and alcohol [28–30]. The hydrophobic hydration structures which form around polymer chains are destroyed by the addition of the salts. PNIPA is probably shrunk into the globule conformation by the addition of the viologen salt. The Stern–Volmer constant (K_{SV}) for the quenching at 15 °C was determined from the initial slope of the plots.

The rate constants for the electron transfer quenching (k_q) are calculated from the Stern–Volmer constant (K_{SV})

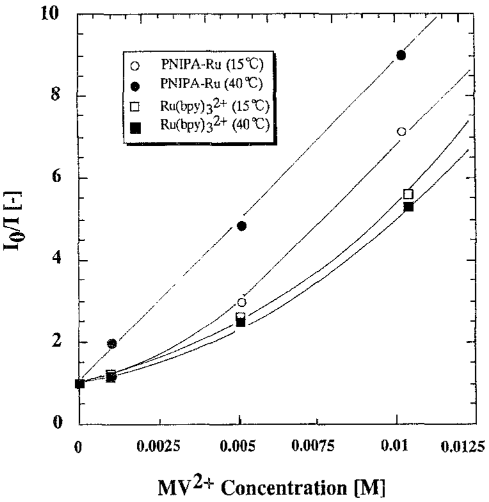
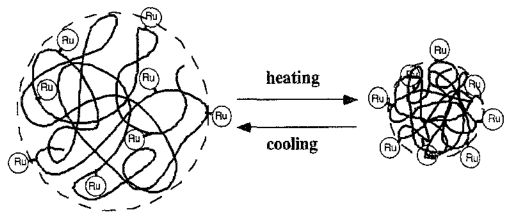


Fig. 4 Stern–Volmer plots for the quenching of PNIPA-Ru and $\mathrm{Ru(bpy)_3^{2+}}$ by viologen at 15 °C and 40 °C

and the lifetime (τ) (Table 2). The rate constant for PNIPA-Ru in the globular state is 4–5 times as large as that in the coil state. This result is quite different from the case of the quenching of PNIPA labeled with pyrene probe (PNIPA-Py) by $\mathrm{MV^{2+}}$ in the previous work. Pyrene group is embedded rigidly into hydrophobic polymer matrix in the globular state. Therefore, ionic quencher $\mathrm{MV^{2+}}$ could not approach pyrene probe in the polymer matrix and then electron transfer quenching is suppressed. Contrary to the pyrene probe, the Ru-probe in PNIPA-Ru is effectively quenched in the globular state more than in the coil state. This means that the Ru-probe is placed at the interface of polymer matrix and bulk water, not embedded into the polymer matrix as shown in the pyrene probe. The $\mathrm{MV^{2+}}$ quencher is concentrated around the polymer globule, resulting in the effective quenching due to increase in the local concentration. The differences in the micro structure of PNIPA-Ru and PNIPA-Py are tentatively illustrated in Fig. 5.

Conclusively, hydrophilic tris(2,2′-bipyridine) ruthenium(II) complex probe was incorporated into poly(*N*-isopropylacrylamide) (PNIPA), which is known to be a thermoresponsive polymer. The electron transfer quenching rate constant (k_q) in a globular state (higher temperature than the LCST (31 °C)) is 4–5 times as large as that in a coil state (lower temperature) from the Stern–Volmer plots. This result is quite different from the quenching of PNIPA labeled with polycyclic aromatic probes like pyrene chromophore. This is because hydrophilic Ru-probe is located at the interface of polymer globular matrix, not embedded into the hydrophobic matrix, even in a globular state. The feature of the globular state of PNIPA can be figured as a soft molecular environ ment, not as a hard hydrophobic matrix.

(a) PNIPA-Ru



(b) PNIPA-Py

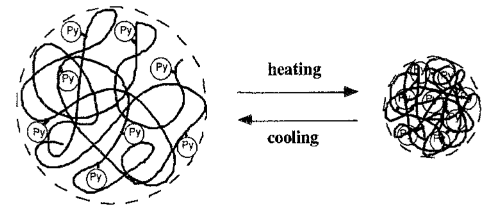


Fig. 5 A tentative illustration for micro structure change of (a) PNIPA-Ru and of (b) PNIPA-Py by phase transition

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